

RAPID GROWTH OF LARGE-SCALE (40–50-CM) KDP CRYSTALS

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Introduction

Work on rapid growth of KDP-type crystals, mainly KH_2PO_4 (KDP) and $\text{K}(\text{D}_x\text{H}_{1-x})_2\text{PO}_4$ (DKDP), was initiated in the early 1980s because the Nova laser at Lawrence Livermore National Laboratory (LLNL) needed large-aperture single-crystal plates. Several rapid growth techniques^{1–3} were developed, and a project was started at LLNL⁴ with a goal of growing KDP-type crystals at more than an order of magnitude faster than the traditional technique. As a result, rapidly grown crystals of about 10 cm were obtained. Nevertheless, the frequency conversion arrays on Nova were constructed from 27- × 27-cm KDP single-crystal plates grown using traditional slow-growth techniques.

The baseline design for Nova's successor—the National Ignition Facility (NIF)⁵—incorporates about 600 41- × 41-cm Pockels cell, doubler, and tripler crystals. Depending on the type of frequency conversion used for the NIF, the boules that would yield crystal plates of this size must be about four times the size of the Nova boules (see Figure 1). Conventionally grown crystals usually grow 1–2 mm/day for KDP crystals and not faster than 1 mm/day for DKDP. At these rates, it can take more than two years to grow a crystal with the size required for NIF. This slow rate and high risk associated with traditional crystal growth techniques stimulated new work on KDP rapid growth at LLNL about four years ago.⁶ Here we describe recent progress in this work including the growth of KDP and DKDP crystals up to 50 × 50 cm² in cross section and grown at rates in excess of 10 mm/day.

Figure 2(b) shows that the final size of a traditionally grown boule is approximately twice as long as it is wide because the regenerated seed and the material with high density of dislocations originating at the seed cap occupy the large portion of the crystal. Additionally, at the low

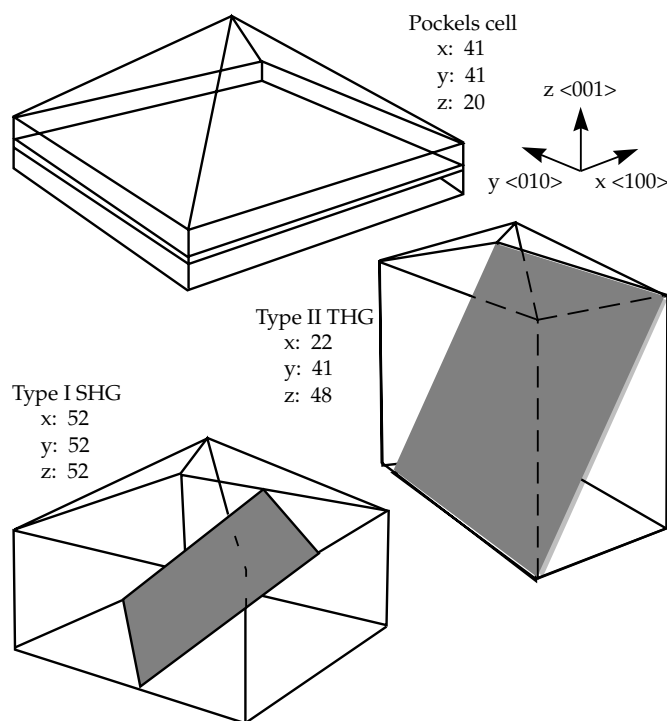


FIGURE 1. The minimum size (centimeter) of KDP single-crystal boules required to obtain Pockels cell and harmonic generation plates of different types for the NIF project. (40-00-0697-0989pb01)

growth rate used in conventional growth, impurities in the starting salt generate a “dead zone,”⁷ a term used to describe an area where growth rates along the <100> and <010> directions are near zero. Attempts to increase growth rates often resulted in the formation of defects on prismatic {100} faces, which start growing at supersaturations just above the “dead zone.” As a result, conventional crystals are grown only in the <001> direction, and the growth of the boule must be preceded by the complicated process of obtaining seeds that have the

cross section of the final crystal [see Figure 2(a)]. This process significantly increases the production time.

The use of very pure salts can reduce the width of the “dead zone.” We have shown^{8,9} that if growth is performed in a regime where the growth rates along $\langle 100 \rangle$ and $\langle 010 \rangle$ are sufficiently high and comparable to that along $\langle 001 \rangle$, defects on those faces do not form, and crystals have high optical quality both in the prismatic and pyramidal sections. For example, the 37-cm crystal plates currently used on Beamlet, the NIF prototype, were grown by the traditional method. Until last year, the size of rapidly grown crystals did not exceed 15–20 cm.

With our work on KDP rapid growth, we now report that we can grow KDP crystals rapidly with up to $50 \times 50 \text{ cm}^2$ in cross section. We used a method based on the use of the “point seed.”¹⁰ In this method the size of the seed does not depend on the final size of the crystal because the crystal grows uniformly on both prismatic $\{100\}$ and pyramidal $\{101\}$ faces [see Figures 2(c) and 2(d)]. While the presence of the prismatic faces and the resulting polysectorality can be a potential source of optical inhomogeneity, our measurements showed the following: crystals grown by this technique (to sizes of 10–15 cm) using high-purity salts and at growth rates of 10–15 mm/day have good optical uniformity. In addition, the entire volume of the crystal can be used for obtaining high-quality plates.⁹

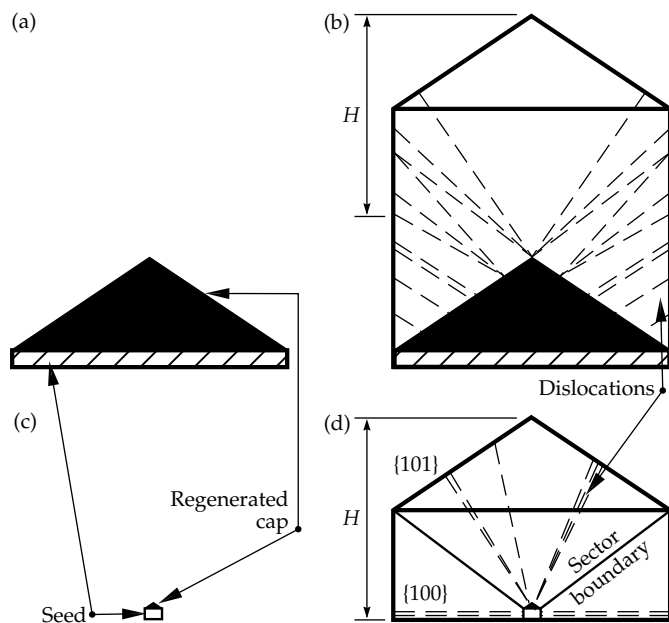


FIGURE 2. Schematic of traditional seed (a) and final traditional crystal (b) compared to rapid-growth point seed (c) and final point-seed crystal (d) with length H for cutting plate. (40-00-0796-1483pb03)

Apparatus

Figure 3 is a schematic of the full-scale rapid growth system, and Figure 4 is a photograph of the same system. The system consists of a 1000-L glass tank submerged in a controlled-temperature water bath. The crystal is grown on a square, $60 \times 60\text{-cm}^2$ acrylic platform; it is rotated alternately in two directions on a symmetrically programmed schedule with controlled acceleration, deceleration, and rotation rates. A seed protector, specially developed for this work, is inserted within the platform shaft where it can freely move up and down, allowing us to keep the 1-cm^3 seed sealed at room temperature while the crystallizer temperature is manipulated. Here, solution treatments, such as filtration and overheating, are executed for any desired length of time while the seed is perfectly preserved under the seed protector. When the solution is ready for growth, the seed protector is raised, and the growth

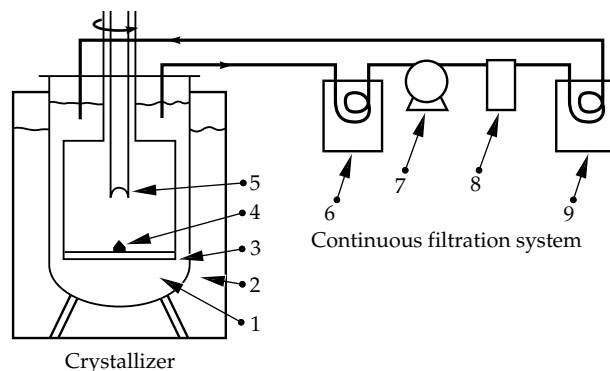


FIGURE 3. Schematic of the 1000-L crystallizer: (1) 1000-L glass growth tank; (2) temperature-controlled water bath; (3) platform; (4) seed; (5) seed protector; (6) heater; (7) pump; (8) filter; (9) cooler. (40-00-0796-1482pb02)

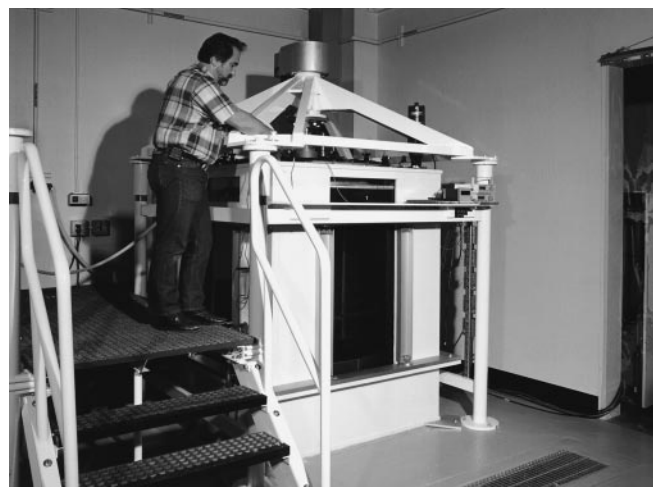


FIGURE 4. Photograph of the 1000-L crystal growth system. (40-00-0697-1068pb01)

process begins. The seed protector can also be used if the crystal needs to be remelted. Once the crystal is melted to the size of the initial seed, it can then be covered by the seed protector, and solution processing can be repeated. In this way, the growth process can be repeated several times without introducing a new seed.

Previously, Montgomery and Milanovich¹¹ showed that high laser-damage thresholds could be obtained in conventionally grown KDP by continuously filtering the solution during growth. The same continuous filtration system was developed in this work for filtration growth solutions at high supersaturation (see Figure 3). Our system contains three temperature-controlled sections: a superheater, a filter (both operating at 80°C), and the third section, where the filtered solution is cooled to the growth temperature. This system has been used to grow KDP and DKDP crystals in small 20-L crystallizers up to a size of 17 cm. This system was also tested in 1000-L tanks, where it will be used after the first 55-cm crystals have been grown.

Solution Stability and Crystal Growth

KDP crystals grow on vicinal hillocks formed by dislocations.⁷ The normal growth rate R of a crystal face growing by this mechanism is given by

$$R = pV, \quad (1)$$

where p is the slope of the dislocation hillock and V is the tangential speed of the elementary steps. According to this formula, there are two ways to increase the growth rate: steepening the hillocks or increasing the step speed. In the kinetic limit, the step speed V has been shown both theoretically^{12,13} and, for many systems, experimentally^{14–16} to be given by

$$V = \omega\beta \Delta C, \quad (2)$$

where ω is the volume per molecule in the solid, $\Delta C = (C - C_0)$ is the absolute supersaturation, C and C_0 are the actual and equilibrium concentrations, respectively, and β is the kinetic coefficient that must take into account the kinetic barriers associated with the multi-stage process of moving solute from the solution into the steps.

The slope of the dislocation hillock in Eq. (1) is given by⁷

$$p = h\varepsilon, \quad (3)$$

where h is the height of the elementary step, and ε is the activity of the dislocation source. The activity ε of

the dislocation source is a function of both the critical radius r_c and the structure of the dislocation source. In the simple case of an isotropic growth spiral, $\varepsilon = m/(19r_c + 2L)$, where m is the number of unit step heights in the dislocation source and $2L$ is the length of the perimeter of the region enclosing all dislocations within $19r_c$ of one another.⁷ In the case of polygonal, anisotropic growth hillocks such as those of KDP, the prefactor of r_c also depends on the relative sizes of the kinetic coefficients for each step direction of the polygon but is independent of the absolute value of β .

The critical radius r_c is given by¹⁷

$$r_c = \frac{\omega\alpha_{2D}}{kT\ell nS}, \quad (4)$$

where α_{2D} is the step-edge free energy per unit step height and S is the ratio of the actual to the equilibrium mole fraction of the crystallizing material. ε and, hence, p can be increased by raising ΔC or temperature, T , or by changing the dislocation structure. Furthermore, atomic-force-microscopy investigations^{18, 19} of growth spirals on KDP {101} surfaces have shown that for $\sigma \gtrsim 5\%$, the slopes of growth hillocks on the {101} face are limited by the presence of strain-induced dislocation cores.¹⁹ The details of the effect of these cores on step structure near the core has been investigated theoretically,^{20,21} and the experimental results and complimentary analysis¹⁹ show that the hillock slope is nearly independent of both supersaturation and dislocation structure because these cores are present. As a result, the growth rate along Z can only be increased significantly by raising ΔC to increase V . The effect of these cores was not observed on the {100} face where m and L vary depending on seed regeneration conditions. These conditions allow us to create dislocation sources of varying activity, thereby obtaining different growth rates on the {100} face at the same temperature and supersaturation. It is possible to vary the ratio of the crystal dimension along Z to that in X and Y ,¹⁰ which is practically important for crystal growth of the sizes in Figure 1.

Our data also show that in our regime of growth, the solution flow can slightly affect the growth rate. While the temperature, dislocation structure, and hydrodynamic conditions can also slightly affect growth rates, increasing the supersaturation to increase V is the only effective way to significantly increase growth rates. However, crystal growth in the region of high supersaturations is not a simple practical task because extraneous crystals from the growth solution tend to precipitate. This condition usually leads to the deterioration of the main crystal and termination of the growth run. This makes the problem of solution stability one of the most important challenges for rapid growth. We define solution stability as the ability of the supersaturated solutions to remain free from spontaneous nucleation during

an induction time τ , which must be, obviously, longer than the growth period.

Our previous work²² in small 5–20-L crystallizers showed that KDP and DKDP supersaturated solutions can be stable against spontaneous nucleation for induction time periods of months at undercoolings of up to 30°C. In addition, during continuous cooling, supersaturations σ of up to 100–130% can be reached. For practical measurements, we used relative supersaturation $\sigma = (C - C_0)/C_0$, where C and C_0 are expressed in weight fraction. We showed that the actual stability of growth solutions is much higher than needed for practical crystal growth (Figure 5). The absence of spontaneous nucleation in small crystallizers (5–20 L in volume) during crystal growth at rates of 10–40 mm/day proves that growth solutions are stable. The seed protector device in 20-L crystallizers allows us to grow KDP crystals at growth rates up to 60–70 mm/day. The growth terminates at

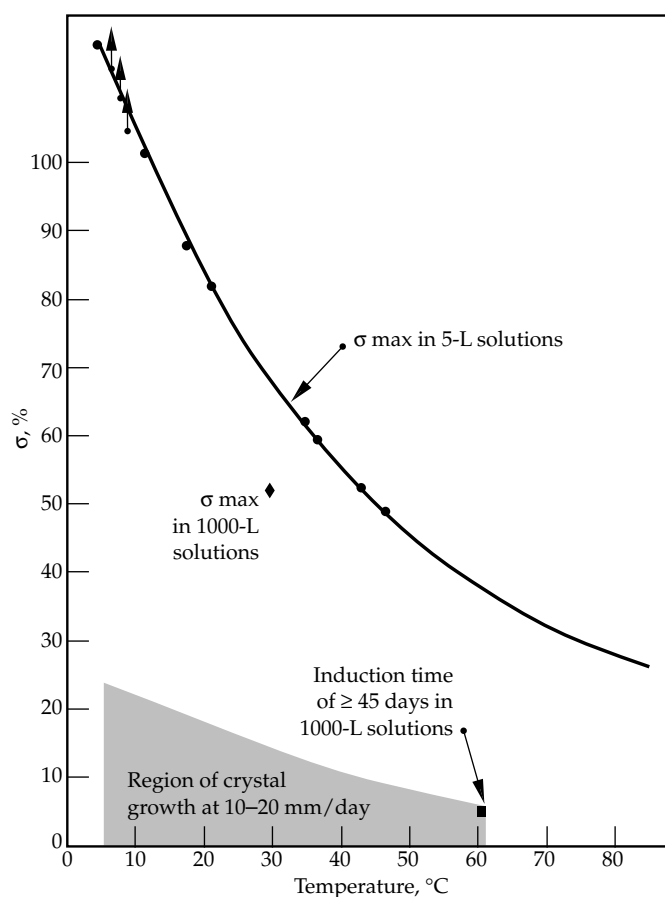


FIGURE 5. Maximum stability obtained in KDP solutions in comparison to the region used for crystal growth. (40-00-0796-1481pb02)

high rates usually because of defects and cracks in the growing crystal, not because of spontaneous nucleation from the solution. We believe that these cracks and defects are caused by impurities or hydrodynamic conditions. These results show that, at the supersaturations needed for practical growth rates (usually not faster than 20 mm/day) in well filtered and overheated solutions, spontaneous nucleation in the solution itself is not a problem. From our observations, any extraneous crystals that appear in the shaded region of Figure 5 are caused by the main crystal either through cracking or moving relative to the crystal holder. Faulty equipment, such as dry surfaces or poorly bonded joints on the platforms, can also cause extraneous crystals to appear.

Our measurements in the 1000-L tanks in Figure 6 gave solution stability of the same order of magnitude: during continuous cooling, σ of about 50% was reached, and the induction time τ in a stirred solution saturated at 65°C was more than 1.5 months at $\sigma = 6\%$. (The run was interrupted to continue crystal growth experiments.) These results furthered our knowledge of the absolute level of the solution stability. We have previously shown²² that we could not measure the induction time in 5-L tanks at $\sigma = 6\%$ because, practically, it was infinite. But if we assume that the probability of homogeneous nucleation is proportional to the volume of the solution, the calculation from a τ of more than 45 days obtained in 1000-L tanks leads us to a τ in 5-L vessels of at least 25 years.

According to the classical nucleation theory,²³ homogeneous nucleation from the solution can start when, as a result of fluctuation, some certain number of molecules create an aggregate with the size of r_c . Simple calculations allow us to estimate the size of a critical nucleus at the values of σ used during growth.

From Eq. (4), using $\omega = 9.68 \times 10^{-2}/\text{nm}^3$ per molecule, $\alpha = 12.9 \text{ mJ}/\text{m}^2$ (Ref. 22) at $T = 30^\circ\text{C}$, and $S = 1.7$, or $\sigma = 57\%$ (the point when mass crystallization from solution occurs), we obtain $r_c = 1.1 \text{ nm}$. At $\sigma = 6\%$ ($S = 1.07$), the same calculation gives us $r_c = 8.6 \text{ nm}$. $r_c = 1.1 \text{ nm}$ corresponds to a critical nucleus containing about 60 KDP molecules ($4\pi r_c^3/3\omega$), while $r_c = 8.6 \text{ nm}$ corresponds to one with about 30,000 molecules. The latter is unlikely to form spontaneously on any time scale, which leads us to conclude that at the relatively low supersaturations used in the rapid growth process, homogeneous nucleation in the bulk cannot take place.

Figure 6 shows one of the large KDP crystals grown in a 1000-L crystallizer compared to a typical 12-cm crystal grown in a 10-L crystallizer. The weight of the large crystal is about 130 kg compared to 1.5 kg for the smaller one. Both crystals were grown on point seeds of the same size. The dimensions of the large crystal are about 45 cm in all X, Y, and Z directions. The entire period of growth was 30 days.

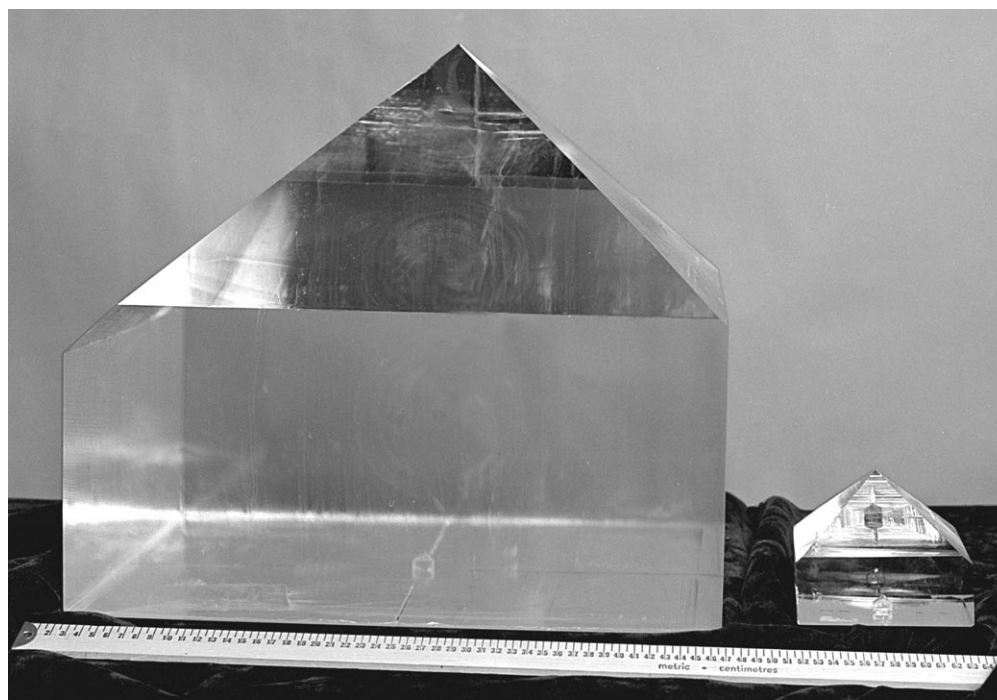


FIGURE 6. Photograph of KDP crystals grown in 1000- and 10-L crystallizers. (40-00-0796-1582pb01)

More than 20 KDP and DKDP crystals with sizes of about 40–50 cm in all directions have been grown. The initial saturation temperature of the solutions in different growth runs varied from 60 to 68°C. According to our calculations, the saturation temperature does not have to exceed 70°C to obtain full-size crystals of about 55 cm on a side and 250 kg in weight from solution volumes of 1000 L. Crystals were grown at rates of 10–25 mm/day along the Z axis and 5–12 mm/day along the X–Y directions. Supersaturation and required cooling rate were controlled by measuring growth rates and crystal dimensions during the growth process.

In the case of the DKDP crystal (Figure 7), the initial saturation point of the solution was 60–66°C, and the deuteration level of the solution was about 92%. The growth rate along the Z axis was about 14 mm/day, and each prismatic face grew at a rate of 10–12 mm/day. Precipitation of the monoclinic phase was never observed during the growth of the tetragonal crystal, which further demonstrates the high stability of the growth solutions against spontaneous nucleation.

At present, the main obstacles in obtaining crystals of the larger size are related to mechanical problems resulting from the large size of the equipment. These problems include deformation of the platform-crystal holder caused by the flow of the solution (1000 kg in mass) and the increasing mass of the crystal as it grows. Though we are working on solving these problems, we are currently growing crystals of sufficient size to provide Z-plates for the NIF.

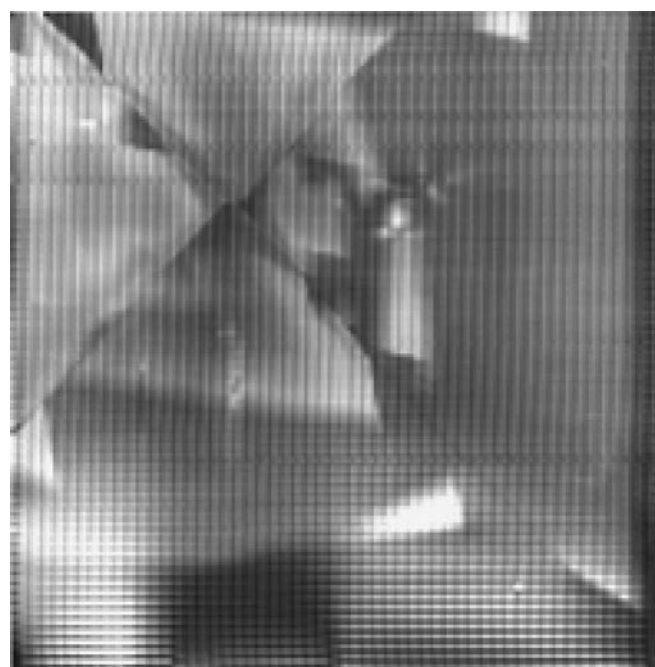


FIGURE 7. Photograph of DKDP crystal with the deuteration level about 92%. The size in cross section is 50 × 50 cm². (40-00-0697-0987pb01)

Crystal Quality

Only preliminary measurements have been performed on the crystals grown in 1000-L crystallizers. Some crystals had no visible defects, though in many crystals, solution inclusions appeared randomly on both the prismatic and pyramidal faces. These defects were typically slight on the prismatic {100} faces and much more pronounced on the top of the pyramidal {101} faces. The nature of these defects is not yet clear and is a subject of current investigations.

The surface structure of the crystals did not differ from that typically observed in the small crystals: each prismatic face had only one growth hillock clearly seen in reflected light from the beginning to the end of growth. Growth hillocks on the pyramidal faces changed more often. One or two hillocks with intervicinal boundaries could be observed at any time on the same face, which is also typical for small crystals.²⁴

One of the large crystals which had a cross section of $44 \times 44 \text{ cm}^2$ was cut into Z <001> plates from which two $41 \times 41 \times 1\text{-cm}$ Pockels cell crystals were fabricated (see Figure 1). Measurements of anomalous birefringence and transmitted wavefront distortion on these plates, as well as measurements of the laser-induced damage threshold on witness samples taken from adjacent positions in the boule, show that the optical quality of these crystals meets the NIF requirements.

Figure 8 is a profile of the depolarization loss measured in a $29 \times 29\text{-cm}$ section of one plate. The average loss is $4 \times 10^{-2}\%$, and the maximum loss is about 0.1%. These numbers are five to ten times smaller than those specified for the NIF. Figure 9 shows the distortion of the transmitted wavefront due to index variations in the bulk of this plate. The peak-to-valley distortion is $<\lambda/4$, and the maximum gradient is $<\lambda/10 \text{ cm}^{-1}$. These values meet the NIF specifications. The measured laser-conditioned damage threshold at the first harmonic (1064 nm) using 7.6-ns pulses is 32 J/cm^2 . When scaled to 3 ns, this value exceeds the NIF requirement for both the Pockels cell and the second harmonic generator. Our preliminary measurements also show no direct dependence of the damage threshold on sectorial structure of the crystals grown on the point seeds. These findings demonstrate that the presence of the prismatic sectors and sector boundaries are not the obstacles for obtaining large single-crystal plates of high optical quality, as was expected many years ago when this work began.²⁵

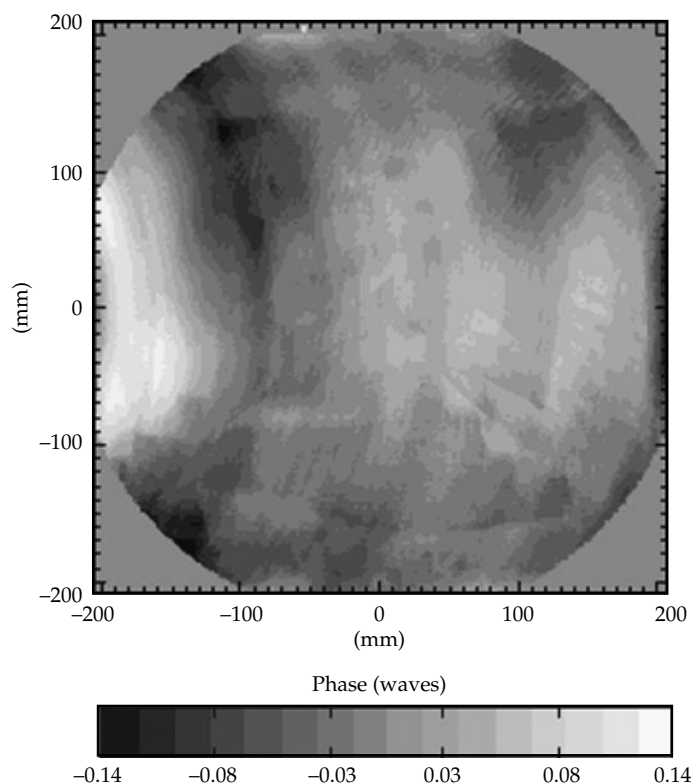


FIGURE 8. Profile of the depolarization loss in a $29 \times 29\text{-cm}$ section of a $41 \times 41\text{-cm}$ plate. Sector boundaries and growth hillock boundaries are clearly visible but result in only minor depolarization losses. (40-00-0697-0988pb01)

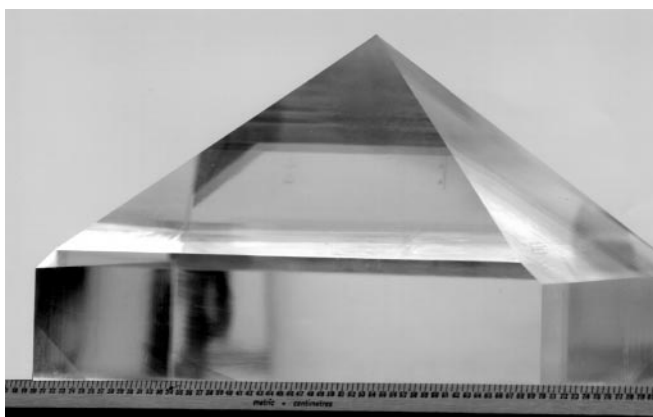


FIGURE 9. Profile of wavefront distortion in a 40-cm circular section of the $41 \times 41\text{-cm}$ plate described in Figure 7. Although sector and growth hillock boundaries are visible, the distortion is small. (40-00-0398-0449pb01)

Conclusion

Our results show that large KDP single crystals for laser fusion systems can be grown rapidly using high supersaturations. The next task of this work is to develop a stable technique for obtaining KDP and DKDP crystals of up to 55 cm that have high optical quality and high laser-damage threshold. The high reproducibility of our results on growth and optical quality has given us a predictive understanding of the rapid-growth technique. We have also shown that we can obtain the desired optical quality in our work with small rapidly grown crystals as well as at large scale. Our current findings lead us to believe that the development of the rapid-growth technique initiated more than 10 years ago is close to a successful conclusion.

Acknowledgments

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